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Copolymers sensitive to temperature and pH in water and in water + oil mixtures: A DSC, ITC and volumetric study

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ABSTRACT

Block copolymer micelles are receiving an increasing interest because of the variety of structures and the possibilities to tune them by changing external and internal parameters achieving the desired properties for a specific purpose. We have investigated the acid/base behavior, self-assembling and solubilization ability towards polar oils of star-like copolymers named Tetronics. They are composed of branched four-arms each one consisting of two blocks made of EO and PO units linked to the diethylenediamine group, which confers pH response ability. The copolymers T1107 and T90R4 were studied with a sequential and reverse architecture. The thermodynamics of the acid/base equilibrium was studied by ITC. The aggregation of T1107 in water was analyzed as functions of pH, composition and temperature. The enhanced oil solubilization in the aqueous T1107 aggregates was widely investigated highlighting the role of the oil structure, composition, temperature and pH. As a general result, the oil induces the copolymer aggregation and the solubilization power of micelles is tunable by changing the pH. Efforts have been devoted to model the calorimetric data in order to achieve the thermodynamic properties of the involved process. Finally, we showed that the Tetronic micelles are more promising than the conventional surfactants micelles because of the larger solubilization power and flexibility of the macromolecular system.

1. Introduction

Polymeric aggregates are valuable pockets to encapsulate hydrophobic materials. Several polymers exhibit self-assembly ability and, some of them, combine the hydrophilic poly(ethylene oxide) block with hydrophobic segments like phospholipids [1], poly(styrene) oxide [2], phenylglycidyl ether [3], poly(propylene oxide) [4,5], etc. The copolymers based on ethylene oxide (EO) and propylene oxide (PO) units belong to two families: (1) the linear poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (named Pluronics) and (2) the branched four-arms each one composed of EO and PO units linked to the diethylenediamine group (named Tetronics). In the last decade, the Pluronics have been receiving a relevant attention because they are no-toxic, their chemical composition can be finely tuned and, finally, they are commercially available. Several physico-chemical investigations of solubilization in these aqueous block copolymer systems were carried out. Kayali et al. [6] used lamellar liquid crystal composed of $EO_{27}PO_{61}EO_{27}$ as solvent in alternative to ethanol to solubilize some fragrance substances (limonene, phenethylalcohol and benzaldeyde). Solubilization, stabilization and delivery of hydrophobic drugs in aggregates of Pluronics were exploited [7–9]. Finally, the affinity of materials environmentally significant [10–15] to Pluronics micelles was investigated.

The prospective of Tetronics has been less explored. These macromolecules are used as disperdent, emulsionants, etc. [16]. Due to their low toxicity, recently, some potentials within the biomedical and pharmaceutical fields emerged [17] being able to incorporate insoluble drugs [18].

Compared to Pluronics, at fixed EO/PO ratio, the Tetronics are more soluble in water; that is ascribable to their peculiar chemical structure determining a large hydrophilicity and, in particular, the EO units distributed along with the chains enhance the solubilization of these compounds [19]. These macromolecules deserve special attention because their micellization behavior is influenced not only by temperature, as Pluronics are, but also by pH variations [18–23] to which Pluronics are insensitive. The features as well as the low cost make these copolymers promising molecules for triggering and controlling the solubilization of additives sparingly soluble in water. The potential application of these systems in various fields, like the drug delivery, the aquifers remediation based on surfactants and so on, requires a deep knowledge and a detailed description of the types of forces exercising between the copolymer micelles and the hydrophobic material. This goal may be achieved by means of thermodynamic tools and overall by calorimetry, which provides a direct measure of the energetic of processes and probes even weak interactions. The present work will be

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developed along this route. Accordingly, extended calorimetric and volumetric experiments will be performed on aqueous solutions of sequential $[(EO)_{57}(PO)_{21}]_2NCH_2CH_2N[(PO)_{21}(EO)_{57}]_2$ and reverse $[(PO)_{17}(EO)_{19}]_2NCH_2CH_2N[(EO)_{19}(PO)_{17}]_2$ copolymers in the absence and the presence of oils prototypes of dense and light non-aqueous phase liquids. To this aim, a number of parameters, *i.e.* oil nature, temperature, pH, concentrations of copolymer and oil, will be varied. Modeling the experimental data will provide insights enabling us to correctly describe the molecular forces controlling these systems.

2. Experimental

2.1. Materials

The Tetronics (from Aldrich) are $[(EO)_{57}(PO)_{21}]_2NCH_2CH_2N[(PO)_{21}(EO)_{57}]_2$ (T1107, 15000 uma) and $[(PO)_{17}(EO)_{19}]_2NCH_2CH_2N[(EO)_{19}(PO)_{17}]_2$ (T90R4, 7200 uma). The standard aqueous solution of HCl (0.1 mol dm^{-3}) is from Carlo Erba. The oils (Aldrich) are dichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1-chloropropane, 1-nitropropane and 1-propanol. All of the products were used without further purification. Water from reverse osmosis (Elga model Option 3) with a specific resistivity greater than 1 MΩ cm was used.

2.2. Densitometry

The measurements of the solutions densities (±3 ppm) were carried out at 298 and 308 K by means of a vibrating tube flow densimeter (Model 03D, Sodev Inc.). The temperature was kept constant within 0.001 K by using a closed loop temperature controller (Model CT-L, Sodev Inc.). The calibration procedure of the apparatus is reported elsewhere [24].

The apparent molar volume ($V_{\Phi,o}$) of the oil in a given mixture was calculated by means of the following equation

$$V_{\Phi,o} = \frac{M}{d} - \frac{10^3(d - d_s)}{m_o d d_s} \qquad (1)$$

where m_o and M are the molality and the molecular weight of the oil, respectively; d and d_s are the densities of the solution and the solvent (water + copolymer) mixture, respectively. The copolymer concentration was maintained constant and the oil molality was systematically changed.

2.3. Isothermal titration calorimetry (ITC)

The ITC measurements were carried out by means of an ultra-sensitive nano-ITC200 calorimeter (MicroCal). The amount of approximately 40 μL was injected into the thermally equilibrated ITC cell (~200 μL). The experimental procedure was set in dependence of the investigated systems as detailed in the following.

2.3.1. Tetronic + water + HCl system

To the aqueous copolymer solution, filling the cell, aliquots (each one being 1 μL) of an aqueous solution of HCl were added. Under the same experimental conditions, the dilution of the copolymer and HCl solutions with water were carried out. The moles ratio between HCl and the copolymer ($R_{HCl/p}$) ranged between 0 and 3. In the case of T1107, three titration curves were determined by using different initial copolymer and HCl molarities.

2.3.2. Tetronic + water system

The study was carried out as a function of temperature (from 307 to 319 K) following two routes. The procedure 1 was based on several independent experiments; each one was done by adding aliquots of an aqueous copolymer solution to water in the cell. Different copolymer concentrations were selected in such a way to investigate both the pre- and the post-micellar regions. The procedure 2 was pursued at 315 K. Namely, in the first titration ca. 40 μl of copolymer solution were added to 200 μl of water; successively, the overloading solution (ca. 40 μl) was removed and a new titration was carried out. The procedure was followed until the measured heat was close to zero.

2.3.3. Tetronic + water + oil system

The experiments were carried out at fixed copolymer composition and changing the oil molarity (M_o). The temperature of 298 K was set because we planned the experiments in such a way that the aqueous copolymer solution was unimeric and micellized in the absence and the presence of the oil, respectively. This route was followed due to the cell/syringe volume ratio constraint, to the sensitivity of the instrument and being that a wide range of M_o should be explored. The experiments were planned as detailed in the following. The syringe was always filled with a given water + T1107 + oil ternary mixture. The cell was filled with the water + T1107 solvent. After the first titration, the overloading solution was removed and a new titration was carried out. The procedure was followed until the measured heat was close to zero.

2.4. Differential scanning calorimetry (DSC)

The measurements were carried out by using the micro-DSC III 106 (SETARAM) under nitrogen flow in the range from 273 to 343 K with a scan rate of 0.6 K min^{-1}. The stainless steel (1 cm^3) sample cell was filled with ca. 500 mg of solution and the reference cell with the corresponding amount of water. The calibration was performed by using naphthalene.

From each thermogram registered within a temperature interval the critical micellar temperature (CMT) was determined as the onset and the maximum of the peak and the enthalpy of micellization (ΔH_M) from the integration of the peak. The baseline was subtracted according to the literature [25]. The CMT and the ΔH_M values are reported in Supporting information.

3. Results and discussion

3.1. Acid/base behavior of Tetronics in water

We believe that the direct determination of thermodynamic functions like enthalpy by means of the calorimetric method is in general the only route to obtain reliable data on the energetics of the studied process. Even if in principle the van‘t Hoffs method may be used to determine the enthalpy change for acid/base equilibria, the accuracy of the equilibrium constant might be of the same order of magnitude of its temperature dependence leading to unreliable value of the computed enthalpy [26].

Fig. 1 shows the trends of the heat of injection corrected for the dilution effects (Q_i) as a function of $R_{HCl/p}$ for the HCl/T90R4 and HCl/T1107 systems. For T90R4 in the dilute domain Q_i is constant to $R_{HCl/p} \sim 0.6$ thereafter it sharply decreases to $R_{HCl/p} \sim 1$ beyond which it monotonically increases reaching a nearly null value. T1107 exhibits a different profile as in the dilute region a maximum is present and from $R_{HCl/p} \sim 1$ Q_i increases in a similar manner as T90R4 does (Fig. 1). The maximum is still present if both the T1107 and HCl concentrations are varied.

The titration performed by using aqueous HCl solution involves the protonation of the two basic centers of the etylenediamine group according to the following schemes

$$\mathrm{T} + \mathrm{H}^+ \rightarrow \mathrm{TH}^+ \qquad (1)$$

$$\mathrm{TH}^+ + \mathrm{H}^+ \rightarrow \mathrm{TH}_2^{2+} \qquad (2)$$